



Complete Accepted: Aug. 23, 1934.

## COMPLETE SPECIFICATION.

### Improved Sterile and Self-sterilizing Cellulosic Fibrous Products.

I, PAUL PICK, of 134, West Street, New York, United States of America, a citizen of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to sterile and self-sterilizing cellulosic fibrous products, and to a method of making the same, intended more particularly for surgical and sterilizing purposes.

It is known that the cultivation of bacteria in water ceases when the latter is introduced into vessels of silver or copper and that, after a few hours in such vessels, the bacteria present are completely killed. This fact has been utilised in the sterilizing vessels known under the registered Trade Mark of "Katadyn" sterilisers. These vessels contain lumps of pumice which have been impregnated with silver salts, and then heated to incandescence in order to reduce the silver salt to metallic silver, which latter, however, is much less finely divided than colloidal silver. It is known, however, to use this latter, either as such or deposited upon a support, for sterilizing water and, in fact, the advantageous sterilizing properties of colloidal silver have been utilized in many ways. Thus it is known to impregnate wood and fabric with it for purposes of protection and it has also been proposed to deposit silver from colloidal solution on to materials used for surgical, medicinal and hygienic purposes, such as for example bandages and wadding, the material thus treated becoming self-sterilizing.

It has been found that cellulose material which has been impregnated with colloidal silver or copper is inclined to lose its colloidal deposit since the adherence between the latter and the cellulose fibre is not very strong and resembles that between the fibre and graphite. The object of this invention is to provide a cellulosic fibrous product impregnated with colloidal silver or copper in which the adherence between the fibre and the metal is much superior to that in

the case of the impregnated fibrous products heretofore known.

According to this invention, the products are made by impregnating with colloidal silver or copper a material, such as fabric or wadding, consisting of cellulose fibre which has been converted to hydrocellulose or oxycellulose to an extent which is indicated below.

When ordinary cellulosic material is subjected to bleaching treatment, the material is bleached without evident chemical or structural modification, but at the same time there is a limit to the resistance exhibited by cellulose towards the oxidizing agents employed in effecting the bleaching, and undue action of the bleaching agent leads to the production of oxycellulose and, in some cases, of hydrocellulose as well. It is to be understood that the conversion to hydrocellulose or oxycellulose referred to above and in the appended statement of claim is carried to a point materially beyond that resulting from normal bleaching operations, but not so far as to destroy the fibrous nature of the structure.

It may be pointed out that care is taken to avoid the production of oxycellulose during the bleaching of cellulosic fibre material; in this connection it is to be noted that, as mentioned above, the adherence of colloidal silver or copper to ordinary cellulose fibre material (e.g. as it appears on the market for surgical use and therefore in a bleached condition) is very unsatisfactory, and it is only when the conversion to oxycellulose (or hydrocellulose) has been carried to materially beyond the stage produced during bleaching that improved adherence results. Oxycelluloses or hydrocelluloses possess a powerful surface attraction for colloidal metals with the result that the colloidal silver or copper in the impregnated product cannot be blown or rubbed off. Colloidal silver or copper spread on oxycelluloses or hydrocelluloses acts in a humid condition as a catalyst of hydrogen peroxide or probably ozone and therefore is self-sterilizing.

The product is made by impregnating the fibrous material (e.g. wadding, tex-

tile material, cotton flannel, etc.) with the colloidal metal. The metal may be deposited on the fibres of the material in the nascent state, this being a very satisfactory way of making the product.

By way of example an electrical method of impregnating the fibrous material is here described, although it must be distinctly understood that the invention is not limited thereto. In this method silver or copper is electrically dispersed in the presence of the fibrous material (which has previously been converted to oxycellulose or hydrocellulose to the extent indicated). Assuming that the metal being deposited on the fibre is silver, two horizontal silver plate electrodes are submerged in water and the fibrous material is placed between them. A current is then passed between the electrodes whilst maintaining the water at an elevated temperature. Thus a voltage of 200 and an amperage of 100 may be employed, and the water kept at the boiling point. However, other voltages and amperages may also be used with satisfactory results. The amount of colloidal silver produced may be ascertained by weighing the electrodes or by removing the cellulose material and weighing it dry. The amount of silver precipitated varies, of course, with the conditions of the experiment (e.g. voltage and amperage), as also does the time required to precipitate a given amount. However, from 1% to 25% by weight of silver may be added to the fibrous material. Usually an addition of 5% is sufficient for producing a satisfactory sterilising effect, but of course any excess of this quantity is immaterial. It may be pointed out that no other chemicals whatever, more particularly no protective colloid, need be added during this impregnating process.

The previously prepared colloidal metal may also be mechanically spread upon the fibrous material.

The products provided by this invention have numerous uses. They are permanently sterile, and in addition they are also capable of exerting a sterilizing effect on other bodies in close contact therewith. The sterilized wadding produced by the invention, for example, acts very antiseptically, like wadding impregnated with sublimate of mercury or iodoform, or other similar poisonous chemicals. It is well known that dressings impregnated with phenol, mercury sublimate, or iodoform, not only frequently produce irritation, but in addition they often cause inflammation, or even necrosis, of the wound. Such deleterious results are never obtained with the products provided by this invention since the latter are per-

fectly neutral, indifferent, insoluble, non-poisonous, tasteless and self-sterilizing, so that they never produce the slightest irritation of the living tissue. The colloidal metals used also are insoluble in organic acid and organic solvents. Practical experiments have shown that the products provided by this invention produce a sterilizing effect on wounds which acts to a depth of 5—10 mms. which is greatly superior to the effect produced with the antiseptic preparations hitherto employed. Colloidal metal wadding also has the advantage over iodoform wadding of being completely odorless; in addition many people suffer from iodide catarrh, cardiac complaints, loss in weight, and even exophthalmic goitre through traces of iodine preparations entering the system and the superiority of colloidal metal wadding in this respect is quite apparent. In fact, products provided by this invention have extensive therapeutical application, not only for application to internal and external wounds, but also in dental and surgical practice (e.g. for filling dental cavities, large cavities resulting from abscesses, etc.). It has been found experimentally that the colloidal metal wadding provided by the invention destroys the bacteria of cholera, dysentery, typhoid fever, influenza, erysipelas, and tetanus, streptococci and staphylococci. Impregnated wadding, or strips of textile material are particularly adapted for therapeutic use. The impregnated wadding may also be combined with adhesive plaster, e.g. rubber plaster, in order to form an emergency dressing.

The use of the products as sterilizing agents, however, is not limited to the therapeutical application described. They may be used as preserving and sterilizing agents for decaying and infected organic matter in contact therewith. The products, such as those made by impregnating wadding or other cellulosic organic tissue which has been partly converted to oxycellulose or to hydrocellulose, may also be used to sterilize water by placing them in bottles or other receptacles used for holding the water. Contaminated water always contains sulphuretted hydrogen which reacts with the sterilizing silver. The colloidal silver wadding provided by this invention is brown, or even reddish brown, and the black product formed on interaction with hydrogen sulphide can therefore be seen at once, so that the strength of the sterilizer can be gauged at once by its colour.

It is to be distinctly understood that the products provided by this invention may consist of any kind of cellulosic fibrous material which has been converted to oxy-

cellulose or to hydrocellulose to the extent indicated and the invention is not limited in this respect. Thus, in addition to the products above-mentioned, 5 paper, linen, (the latter in strip form, for example) may enter into the composition of the products provided by the invention.

10 Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

15 1. A method of making a sterilizing and self-sterilised cellulosic product, more particularly for surgical and sterilizing purposes, consisting in impregnating with colloidal silver or copper a material such as fabric or wadding, consisting of cellulose fibre which has been converted to 20 hydrocellulose or to oxycellulose to the extent hereinbefore indicated.

2. A method as claimed in claim 1 in

which the colloidal silver or copper is precipitated in the nascent state in the 25 presence of cellulosic fibre material.

3. A method as claimed in claim 1 in which the colloidal silver or copper is mechanically spread upon the cellulosic fibre material. 30

4. The use of the method claimed in any one of the preceding claims for making a water sterilizer, more particularly from wadding which has been converted to oxycellulose or to hydrocellulose 35 to the extent indicated, for filling into bottles and like receptacles.

5. Sterilizing and self-sterilized cellulosic fibrous material, such as for example fabric, textile material, and wadding, or articles made therefrom, more particularly for the purposes hereinbefore set 40 forth, made by the process hereinbefore described and claimed.

Dated this 30th day of April, 1933.

MARKS & CLERK.